

Spin-orbit and Jahn-Teller Effects in the Excited States of Platinum II Porphyrins

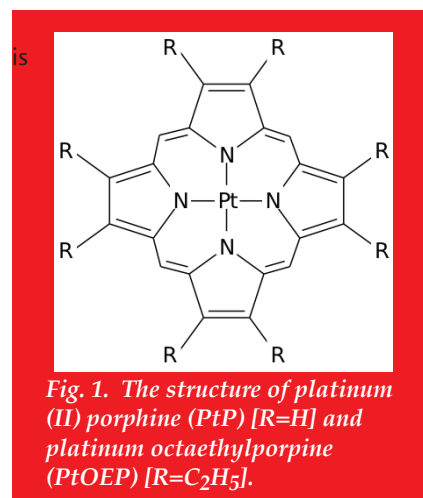
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The manipulation of the spin degrees of freedom in materials poses fundamental questions for research and represents a very promising area for future device applications. Most work to this point has centered on controlling spin in a traditional electronic semiconductor context. However, organic semiconductors are of great interest as the active layer in spintronic devices because they are composed of light elements with weak spin-orbit interactions and thus are expected to have long spin lifetimes.

In order to understand and manipulate electron spin in organic molecules and devices, we have been developing optical probes that use established spectroscopic techniques for detection. This development entails adding heavy elements with strong spin-orbit coupling to achieve the coupling of spin and optical properties. Thus we also need to understand the optical properties of metal-organic molecules.

The experimental component of this team surveyed a variety of polymer hosts and metal-organic compounds and found two promising materials: metal-organic Platinum(II) Octaethylporphine (PtOEP) (Fig. 1) and the polymer poly (9,9-dioctylfluorenyl-2,7-diyl) (PFO). They then measured the photoluminescence (PL) of PtOEP in PFO matrix as a function of magnetic field and temperature, and found that the zero phonon peak at 643 nm goes away as the temperature is lowered from 20 K to 2 K (Fig. 2). The application of a magnetic field restores the zero phonon peak at 643 nm. Light emission was observed with a net circular polarization from PtOEP and is a clear indication of spin-polarized states in this molecule. The data also exhibits Zeeman splitting and thermal/magnetic activated behavior.

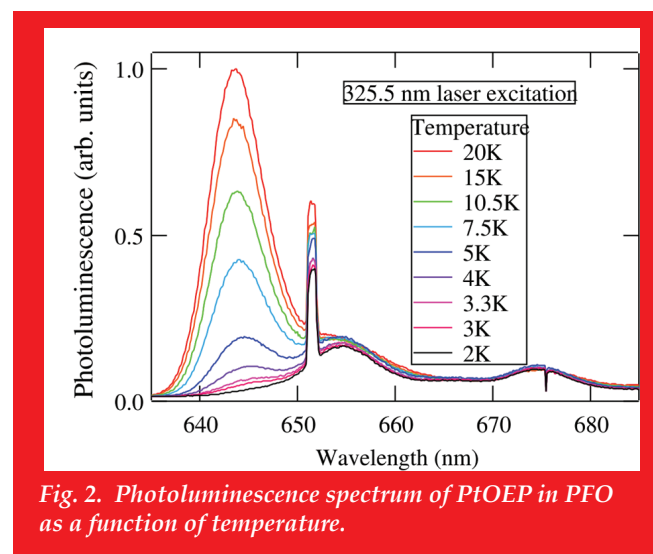
In order to explain the experimental observation we developed a theoretical model. The photoluminescence spectrum of the platinum (II) porphyrins arise from the transition between the lowest triplet excited state and the singlet ground state. The lowest triplet state is spatially doubly degenerate and suffers from a Jahn-Teller instability. We treat the Jahn-Teller problem by reducing the original 105-dimensional Jahn-Teller Hamiltonian to an effective two-dimensional one, whose



effective potential energy surface (PES) determined by hybrid DFT calculations (Fig. 3). By explicit calculation of the intrinsic reaction path connecting the stationary points, we developed an effective one-dimensional PES for the pseudo-rotational motion around the conical intersection (on the bottom of the trough).

From the optimized geometries and associated vibrational frequencies of the singlet ground state, and the excited triplet state, we compute emission transition intensities using the Huang-Rhys approximation. The results of

these calculations, compared with the experimental data, are shown in Fig. 4. The calculation is not broadened by disorder or thermal effects that are implicit in the experimental data. The calculation describes the spectrum well both in the location and relative strengths of the peaks.



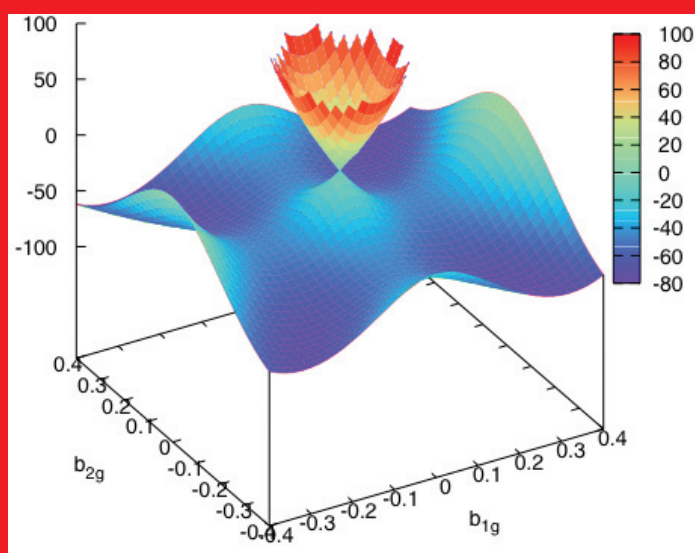


Fig. 3. Effective two-dimensional Jahn-Teller PES.

In order to account for the spin-orbit interaction, we developed spin-orbit time-dependent DFT (SO-TD-DFT), which we used to compute the spin-orbit splitting of the first triplet excited state along the effective one-dimensional Jahn-Teller PES. The lowest state is dark everywhere along that path (no singlet mixing with it), and the next spin-orbit state is bright. The splitting between the lowest (dark) spin-orbit state and the bright spin-orbit state varies along the path from 1.3 K to 7.4 K, in agreement with the experimentally observed behavior (Fig. 2). The SO-TD-DFT code will be made available to the community through the Gaussian software.

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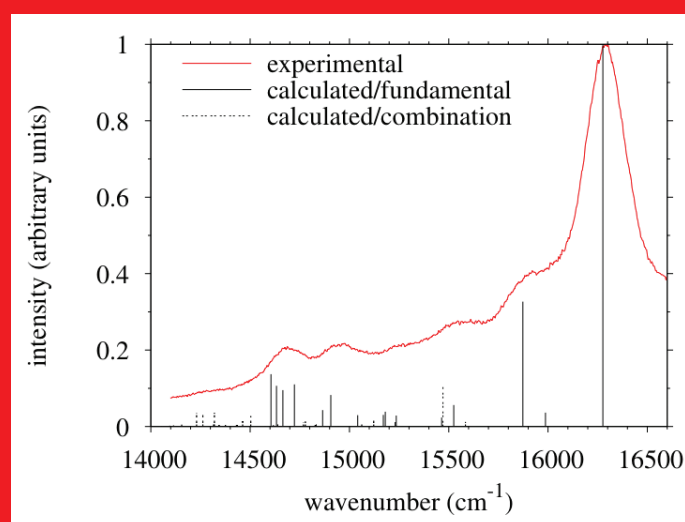


Fig 4. Comparison of experimental and computed photoluminescence spectra of platinum porphine. Experiment: at 85 K, in octane; computation: gas phase, hybrid DFT.